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Historical records of atmospheric Pb deposition in four Scottish ombrotrophic peat bogs: An isotopic comparison with other records from western Europe and Greenland

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[1] Cores collected from ombrotrophic peat bogs in west central, east central, northeast and southwest Scotland were dated (^{14}C , ^{210}Pb) and analyzed (ICP-OES, ICP-MS) to derive and compare their historical records of atmospheric anthropogenic Pb deposition over the past 2500 years. On the basis of Pb isotopic composition (e.g., $^{206}\text{Pb}/^{207}\text{Pb}$), clear indications of Pb contamination during the pre-Roman/Roman, post-Roman and medieval periods were attributed to the mining and smelting of Pb ores from Britain and elsewhere in Europe. Between the 17th and early 20th centuries, during the industrial period, the mining and smelting of indigenous Scottish Pb ores were the most important sources of anthropogenic Pb deposition at three of the sites. In contrast, at the most southerly site, influences from the use of both British Pb ores and imported Australian Pb ores (in more southern parts of Britain) since the late 19th century were evident. At each of the sites, Australian-Pb-influenced car exhaust emissions (from the 1930s to late 1990s), along with significant contributions from coal combustion (until the late 1960s and onset of the postindustrial period), were evident. Atmospheric anthropogenic Pb deposition across Scotland was greatest (~ 10 to $40 \text{ mg m}^{-2} \text{ a}^{-1}$) between the late 1880s and late 1960s, increasing southward, declining to 0.44 to $5.7 \text{ mg m}^{-2} \text{ a}^{-1}$ by the early 2000s. The records from four peat bogs extend knowledge of the chronology of atmospheric Pb deposition trends across the northern hemisphere, there being general agreement with other environmental archive records from not only Scotland but also other countries in western Europe and Greenland. Nevertheless, during all periods investigated here, the isotopic composition of atmospheric Pb deposition across western Europe and Greenland exhibited variations in the relative importance of different sources of anthropogenic Pb, as well as some differences in timings and magnitudes of anthropogenic Pb contamination, arising from variations in local and regional sources of Pb deposition and possibly climatic regimes.

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1. Introduction

[2] Extensive large-scale atmospheric Pb contamination of the northern hemisphere has occurred over several thousand years [Nriagu, 1996], as demonstrated by long-term records from environmental archives such as ice deposits, lake sediments and ombrotrophic peat bogs. The first such studies carried out using Greenland ice [Murozumi *et al.*, 1969; Boutron and Patterson, 1986; Boutron *et al.*, 1991, 1994; Hong *et al.*, 1994; Rosman *et al.*, 1997] and Swedish lake sediment [Renberg *et al.*, 1994; Brännvall

et al., 1997] records all showed pronounced peaks in Pb deposition during the height of the Roman Empire ~ 2000 years ago, a decline during the Dark Ages, a renewed increase during the medieval period and a major increase to maximum levels of Pb deposition during the industrial era. These changes in Pb deposition were generally synchronous with those found in the global Pb production history reconstruction [Settle and Patterson, 1980].

[3] Ombrotrophic peat bogs, like lake sediments, are widely distributed throughout the northern hemisphere but they have the advantage over the latter in that they receive all natural and anthropogenic inputs solely from the atmosphere. Recent studies of long-term atmospheric Pb deposition records in European peat bogs from Sweden [Brännvall *et al.*, 1997; Klaminder *et al.*, 2003], England [Lee and Tallis, 1973; West *et al.*, 1997; Le Roux *et al.*, 2004], Switzerland [Weiss *et al.*, 1997; Shotyk *et al.*, 1998]

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and Spain [Martinez-Cortizas *et al.*, 1997, 2002] found similar trends to those in the Swedish lake sediments and Greenland ice. Renberg *et al.* [2001] suggested that the atmospheric deposition of Pb could be used as a chronological marker in peat deposits in Europe, as the dates A.D. 0, A.D. 1000–1200 and A.D. 1970 could be inferred using the characteristic Roman peak, medieval increase and industrial peak, respectively. Major limitations, however, were suggested to be the specific regional/local differences in the Pb pollution history within Europe. The specific timing and intensity of changes in long-term atmospheric Pb deposition in European peat bogs vary regionally, e.g., Roman peaks in Spanish bogs are more pronounced than those in more northerly European bogs and medieval increases are generally strongest in central Europe and less visible in Spain [Bindler, 2006]. Also, in contrast to these European peat bog records which documented a gradual increase and decrease in ancient atmospheric Roman Pb pollution, Schettler and Romer [2006] found high variability in the influx of Roman Pb in lake sediments from An Loch Mór in western Ireland, attributable to changes in the paleoclimatic regime that favored or limited the wind transport of Pb emissions from ancient smelting sites, rather than changes in the Roman mining and smelting activities.

[4] As relatively few long-term ombrotrophic peat bog records of Pb contamination in Scotland exist [Weiss *et al.*, 2002; Shotyk *et al.*, 2004; Cloy *et al.*, 2005], the main objectives of this work were to provide much more comprehensive historical data for Scottish peat bogs, representing up to 2500 years of deposition, and also, through isotopic comparison with other environmental archives from western Europe and Greenland, to extend our knowledge of the chronology and sources of atmospheric Pb deposition trends across the northern hemisphere.

2. Materials and Methods

2.1. Sampling Sites and Sample Collection

[5] Figure 1 shows the locations of the four ombrotrophic peat bogs from which cores were collected: Flanders Moss (FM), west central; The Red Moss of Balerno (RM), east central; Turclossie Moss (TM), northeast; and Carsegowan Moss (CM), southwest Scotland. Cores were collected at various times between 2001 and 2004 (Table 1) from moss hummocks on domed parts of the bogs using either a monolith tin (M: 50 cm × 15 cm × 7 cm), which was inserted into the vertical face of a freshly dug pit, and/or a Cuttle and Malcolm [1979] corer (CM: 1 m × 5 cm × 5 cm) pushed vertically into the bog. The M and CM cores, ranging from 33 to 112 cm in length, were sliced on site into sections ranging from 1 to 3 cm in thickness and then taken to the laboratory for processing. Core identification codes and collection details are indicated in Table 1. The TM04CM-4 core was collected from the bottom of the pit from which the TM04M-1 core had been previously taken.

2.2. Sample Preparation

[6] The wet peat sections were weighed, air-dried at 30°C, reweighed and then ground using a mortar and pestle. The remaining moisture content of each air-dried peat

section was determined on subsamples by oven drying at 105°C and the residual ash content was estimated by weighing air-dried subsamples (subsequently corrected for moisture content) before and after ashing at 450°C for 4 h. Subsamples (~0.25 g) of air-dried peat (subsequently corrected for moisture content) were digested using a modified US EPA Method 3052 Protocol microwave-assisted HF-HNO₃ digestion method [Yafa *et al.*, 2004; Yafa and Farmer, 2006]. Digests were evaporated to 1 mL on a hotplate and then made up to 25 mL with 2% (v/v) HNO₃. Aristar (VWR, Poole, UK) grade HNO₃ (69%) and HF (48%) and high-purity water (18.2 MΩ cm) from a Milli-Q water system (Millipore, Watford, UK) were used in sample preparation.

2.3. Sample Analysis

[7] With the exception of the highest concentrations (FM01CM-1, 0–33 cm; FM04-1-M, 0–33 cm; RM03CM-1, 0–31 cm; RM03CM-2, 0–32 cm; the combined TM04M-1 and TM04CM-4 cores, 0–55 cm; CM04CM-1, 0–52 cm; CM04M, 0–32 cm), which were measured by ICP-OES, Pb was determined in the prepared 2% (v/v) HNO₃ solutions by ICP-MS. A Thermo Jarrell Ash IRIS ICP-OES (Thermo Electron, Cambridge, UK), equipped with a cross-flow nebulizer and autosampler, was used to determine Pb and Ti concentrations in duplicate sectional samples from FM01CM-1, RM03CM-1, RM03CM-2 and half of the CM04CM-1 core samples. A Perkin Elmer Optima 5300 DV ICP-OES (Perkin Elmer, Beaconsfield, UK), equipped with a gem-cone cross-flow nebulizer and AS 93 plus autosampler, was used to determine Pb and Ti concentrations in duplicate sectional samples from TM04CM-4 and the bottom half of CM04CM-1 and single sectional samples from FM04-1-M, TM04M-1 and CM04M. A PlasmaQuad (PQ) 3 ICP-MS (Thermo Electron, Winsford, UK), equipped with a Meinhard nebulizer, nickel sampler and skimmer cones, Gilson autosampler and a Gilson Minipuls 3 peristaltic pump (Anachem, Luton, UK), was used to determine concentrations in single sectional samples from each of the cores. Calibration solutions were prepared daily by adequate dilution of the relevant stock solutions containing 1000 mg L⁻¹ of the element of interest. Overall analytical precision (±1 RSD) for Pb and Ti determination in duplicate samples by ICP-OES was ≤±5% while analytical precision for ICP-MS determination of Pb in single samples was ≤±8%. For the determination of Pb isotopic ratios by ICP-MS, a solution of the National Institute of Standards and Technology (NIST) common Pb isotopic reference standard SRM 981 (²⁰⁶Pb/²⁰⁷Pb = 1.093, ²⁰⁸Pb/²⁰⁶Pb = 2.168, ²⁰⁸Pb/²⁰⁷Pb = 2.370) was used for calibration and mass bias correction [Farmer *et al.*, 2000]. Analytical precision on these ratios was typically <±0.3%. To ensure the quality of analytical procedures and data, six different reference materials were analyzed along with the samples: Ombrotrophic Peat (NIMT/UOE/FM001) [Yafa *et al.*, 2004], Canadian Peat (1878 P) [Barbante *et al.*, 2000], Bush Branches and Leaves (DC73349), Peach Leaves (GBW 08501), Coal (BCR CRM No. 4) and Coal (NBS SRM 1635). Measured and certified/information only values, where available, for Pb and Ti concentrations in the six reference materials were in good

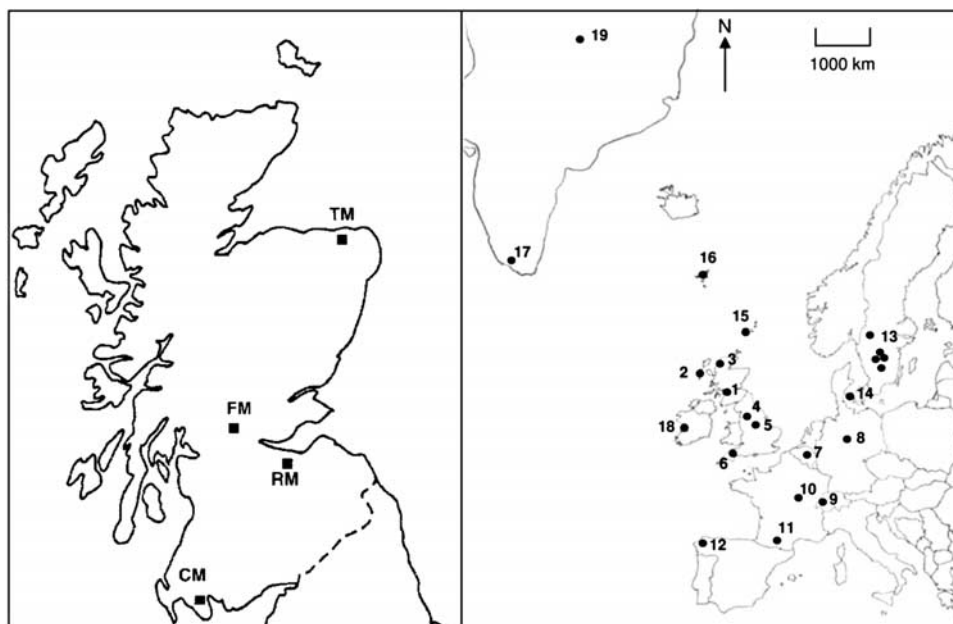


Figure 1. (left) Map of Scotland showing locations of the four peat bog sampling sites, Flanders Moss (FM), Red Moss of Balerno (RM), Turclossie Moss (TM) and Carsegowan Moss (CM). (right) Map of western Europe and Greenland showing the locations of previously studied peat bogs (1, South Drumbo Hill, central Scotland [MacKenzie *et al.*, 1998]; 2, North Uist bog, northwest Scotland [MacKenzie *et al.*, 1997]; 3, Loch Laxford, northwest Scotland [Weiss *et al.*, 2002]; 4, Lindow bog, central England [Le Roux *et al.*, 2004]; 5, Featherbed Moss, central England [Lee and Tallis, 1973]; 6, Tor Royal, southwest England [West *et al.*, 1997]; 7, Misten bog, southeast Belgium [De Vleeschouwer *et al.*, 2007]; 8, Sonnenberger Moor, central Germany [Kempter and Frenzel, 2000]; 9, Etang de la Gruère, west Switzerland [Shotyk *et al.*, 1998]; 10, Port-des-Lambert, central France [Monna *et al.*, 2004a]; 11, Quinto Real, southwest France [Monna *et al.*, 2004b]; 12, Penido Vello bog, northwest Spain [Martinez-Cortizas *et al.*, 1997, 2002; Kylander *et al.*, 2005]; 13, Store Mosse, Trolls Mosse, Öneby Mosse, Dumme Mosse and Traneröd Mosse, south Sweden [Brännvall *et al.*, 1997; Klaminder *et al.*, 2003]; 14, Storelung Mose, Denmark [Shotyk *et al.*, 2003]; 15, Fleck's Loch, Shetland [Shotyk *et al.*, 2004]; 16, Myrarnar, Faroe Islands [Shotyk *et al.*, 2005]; 17, Tasiusaq bog, south Greenland [Shotyk *et al.*, 2003]), lake sediments (18, An Loch Mór, west Ireland [Schettler and Romer, 2006]), and ice deposits (19, Summit, Greenland [Hong *et al.*, 1994; Rosman *et al.*, 1997]).

agreement (Table 2). The isotope ratios of $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ determined in the ombrotrophic peat reference material as 1.176 ± 0.002 , 2.094 ± 0.006 and 2.461 ± 0.007 , respectively, ($n = 59$, ± 1 SD) were in good agreement with corresponding “information only” values of 1.176 ± 0.001 , 2.092 ± 0.002 and 2.461 ± 0.003 [Yafa *et al.*, 2004].

2.4. Age Dating

2.4.1. Lead-210

[8] Analyses for ^{210}Pb , ^{226}Ra and ^{137}Cs were performed by gamma spectrometry using low-background, planar high-purity Ge gamma photon detectors, with a Canberra detector being used for an adjacent core FM01CM-2, collected at the same time as FM01CM-1 [Farmer *et al.*, 2006], and an EG&G Ortec detector for the FM04-1-M,

Table 1. Collection Details for Peat Cores

Site	Latitude and Longitude	Core Identification Code	Collection Date (Month/Year)	Length, cm	Section Thickness, cm	Cross-Sectional Dimensions, cm \times cm
Flanders Moss (FM)	56°09'N, 4°12'W	FM01CM-1	09/2001	106	1	5 \times 5
		FM04-1-M	10/2004	33	3	20 \times 10
The Red Moss of Balerno (RM)	55°51'N, 3°20'W	RM03CM-1	06/2003	83	2	5 \times 5
		RM03CM-2	06/2003	96	2	5 \times 5
Turclossie Moss (TM)	57°37'N, 2°11'W	TM04M-1	08/2004	47	2	15 \times 12
		TM04CM-4	08/2004	112	2	5 \times 5
Carsegowan Moss (CM)	55°12'N, 2°43'W	CM04CM-1	05/2004	106	2	5 \times 5
		CM04M	05/2004	50	2	15 \times 9

Table 2. Mean Pb and Ti Concentrations in Certified Reference Materials

Material	Measured Pb Concentration, mg kg ⁻¹ (± 1 SD)	Certified Pb Concentration, mg kg ⁻¹	Measured Ti Concentration, mg kg ⁻¹ (± 1 SD)	Certified or Information-only Ti Concentration, ^a mg kg ⁻¹
Ombrotrophic peat (NIMT/UOE/FM001)	173 \pm 11 ($n = 67$)	174 \pm 8	391 \pm 25 ($n = 66$)	(357 \pm 18)
Canadian peat (1878 P)	70.9 \pm 4.7 ($n = 10$)	78.8 \pm 2.9	370 \pm 23 ($n = 10$)	...
Bush branches and leaves (DC73349)	44 \pm 3 ($n = 14$)	47 \pm 3	90 \pm 4 ($n = 14$)	95 \pm 20
Peach leaves (GBW 08501)	0.99 \pm 0.10 ($n = 10$)	0.99 \pm 0.08	36.9 \pm 3.0 ($n = 12$)	...
Coal (BCR CRM No. 40)	23.0 \pm 2.0 ($n = 5$)	24.2 \pm 1.7	764 \pm 63 ($n = 6$)	...
Coal (NBS SRM 1635)	2.0 \pm 0.2 ($n = 5$)	1.9 \pm 0.2

^aInformation-only concentration indicated by parentheses.

RM03CM-1, TM04M-1 and CM04M cores. Air-dried subsamples weighing from ~ 1 –20 g were sealed in polycarbonate containers, which were then stored for a minimum of three weeks before analysis in order to allow ^{222}Rn to come to radioactive equilibrium with ^{226}Ra . Detection efficiencies were determined for each counting geometry using standards prepared by spiking appropriate weights of peat, which had nondetectable activities of the nuclides of interest, with

known activities of ^{210}Pb , ^{226}Ra , and ^{137}Cs using certified standard solutions (Amersham plc). The standards were then prepared in the same geometry as the samples. The constant rate of supply (CRS) model [Appleby *et al.*, 1997] was applied to ^{210}Pb inventories calculated from the unsupported ^{210}Pb data to generate age dates for sections in FM04-1-M [Cloy *et al.*, 2005], RM03CM-1, TM04M-1, and CM04M. In the case of the FM01CM-1, RM03CM-2,

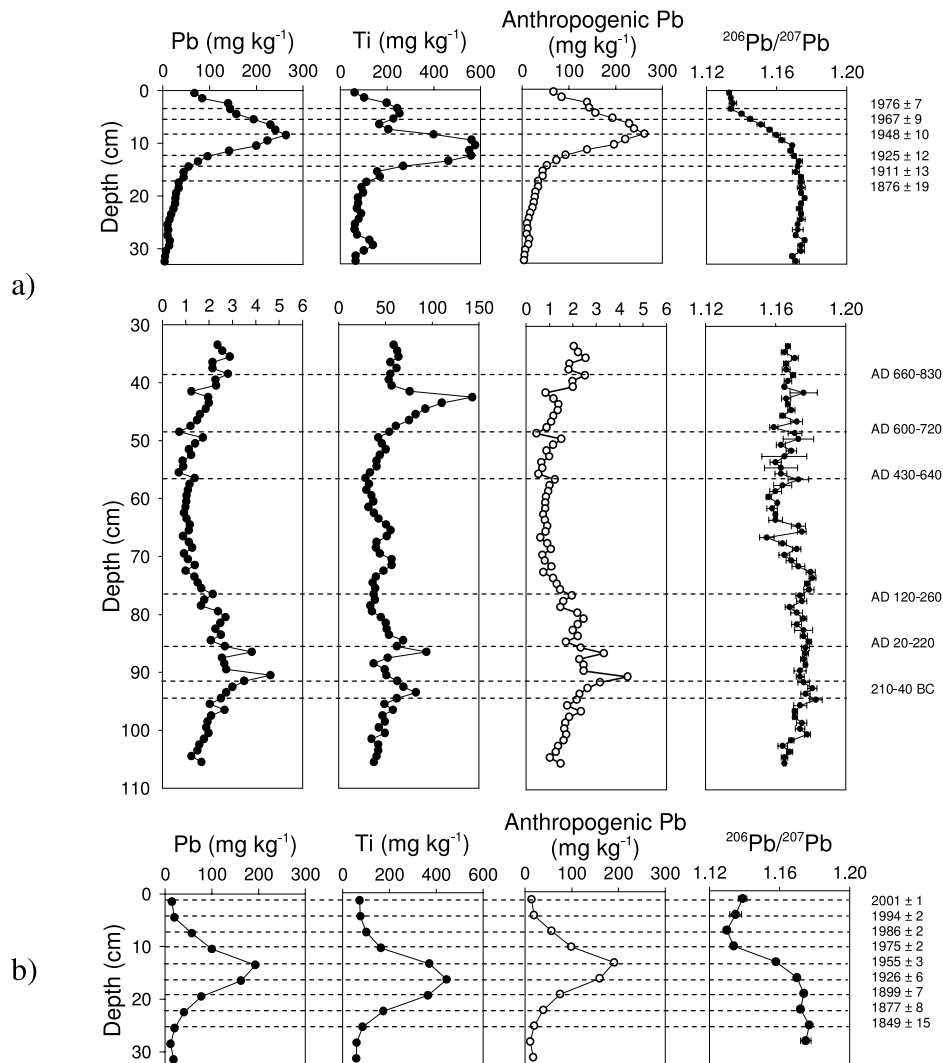


Figure 2. Profiles of Pb, Ti, and calculated anthropogenic Pb concentrations (calculated relative to Ti) (mg kg⁻¹) and measured $^{206}\text{Pb}/^{207}\text{Pb}$ ratio (a) in the ^{210}Pb - and ^{14}C -dated Flanders Moss FM01CM-1 core and (b) in the ^{210}Pb -dated Flanders Moss FM04-1-M core.

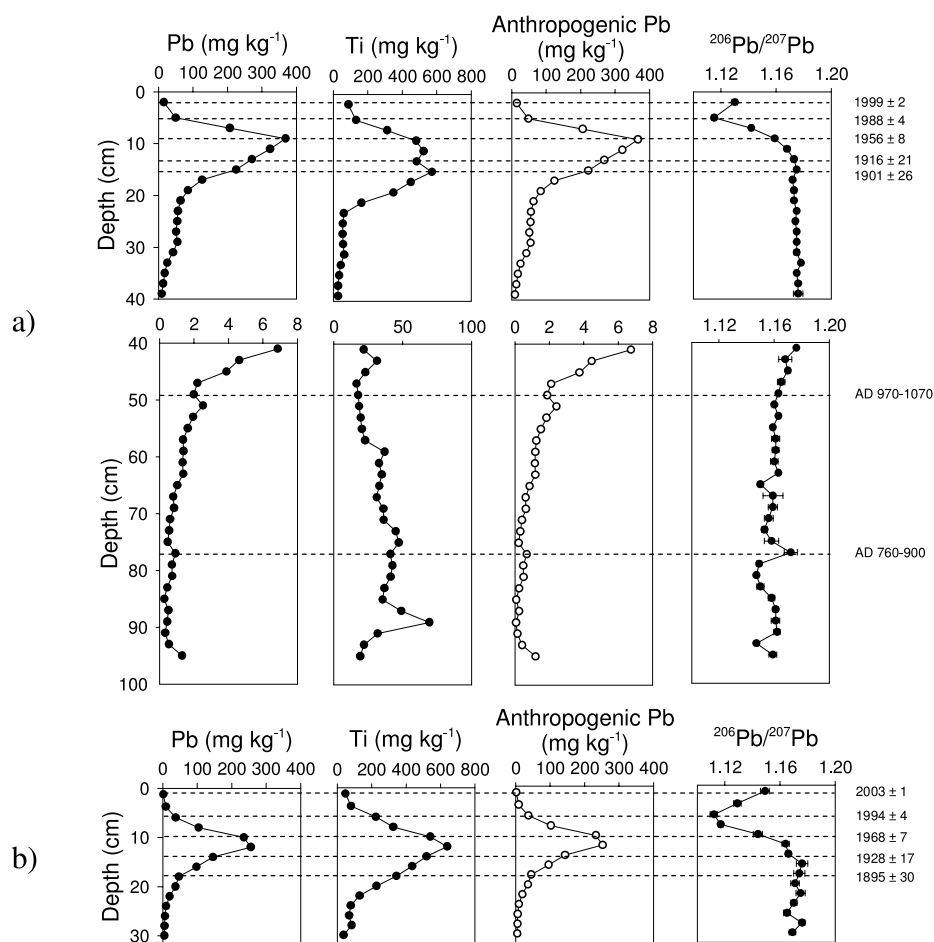


Figure 3. Profiles of Pb, Ti, and calculated anthropogenic Pb concentrations (calculated relative to Ti) (mg kg⁻¹) and measured ²⁰⁶Pb/²⁰⁷Pb ratio (a) in the ²¹⁰Pb- and ¹⁴C-dated Red Moss of Balerno RM03CM-2 core and (b) in the ²¹⁰Pb-dated Red Moss of Balerno RM03CM-1 core.

and CM04CM-1 cores, ²¹⁰Pb dates were obtained by extrapolation, aided by matching of ²⁰⁶Pb/²⁰⁷Pb profiles, from data from the appropriate sister cores, FM01CM-2 [Farmer *et al.*, 2006], RM03CM-2, and CM04M, collected on the same date.

2.4.2. Carbon-14

[9] Humic acid fractions from selected deep peat sections from the FM01CM-1, RM03CM-2, TM04CM-4 and CM04CM-1 cores were extracted using a standard acid-base-acid pretreatment procedure [Cook *et al.*, 1998] and ¹⁴C dated by accelerator mass spectrometry (AMS) using the SUERC AMS facility (NEC 5 MV terminal voltage instrument) operated at 4.5 MV and with carbon in the 4+ charge state. The ¹⁴C ages were calibrated to calendar age ranges using the Oxford Radiocarbon Accelerator Unit calibration program (OxCal ver 3) [Bronk Ramsey, 1995].

3. Results

[10] Total Pb and Ti (used as a conservative, soil dust-related element [Shotyk *et al.*, 2001, 2002a]) concentrations, calculated anthropogenic Pb concentrations (calculated relative to Ti using the Pb/Ti ratio of 0.00545 for the upper continental crust [Wedepohl, 1995]) and measured

²⁰⁶Pb/²⁰⁷Pb ratio profiles, including age dates, for the FM, RM, TM and CM cores are shown in Figures 2, 3, 4, and 5, respectively. The anthropogenic Pb concentrations so calculated are estimates of Pb enrichment as there may be differences in local geology affecting the natural Pb/Ti ratios at the four sites. The FM site has been the subject of previous investigations [Farmer *et al.*, 1997, 2006; MacKenzie *et al.*, 1997; Cloy *et al.*, 2005] and some results from FM01CM-1 and FM04-1-M have been presented elsewhere [Cloy *et al.*, 2005; Farmer *et al.*, 2006]. It was found that the top of the FM01CM-1 core did not equate to the surface of the bog and A.D. 2001 because of the loss of some material during core collection [Farmer *et al.*, 2006].

3.1. Total Pb Concentration Profiles

[11] Near the bottom of the FM01CM-1 and TM04CM-4 cores, peaks in total Pb concentration occurred between depths of 102 and 71 cm and 145 and 113 cm, respectively, with mean values of 2.33 ± 0.75 mg kg⁻¹ and 1.98 ± 0.56 mg kg⁻¹, respectively (see Figures 2a and 4). On the basis of available ¹⁴C dates, these peaks occurred between ca. 200 B.C. and A.D. 200. The lowest measured mean total Pb concentrations (and their corresponding depths), in each of

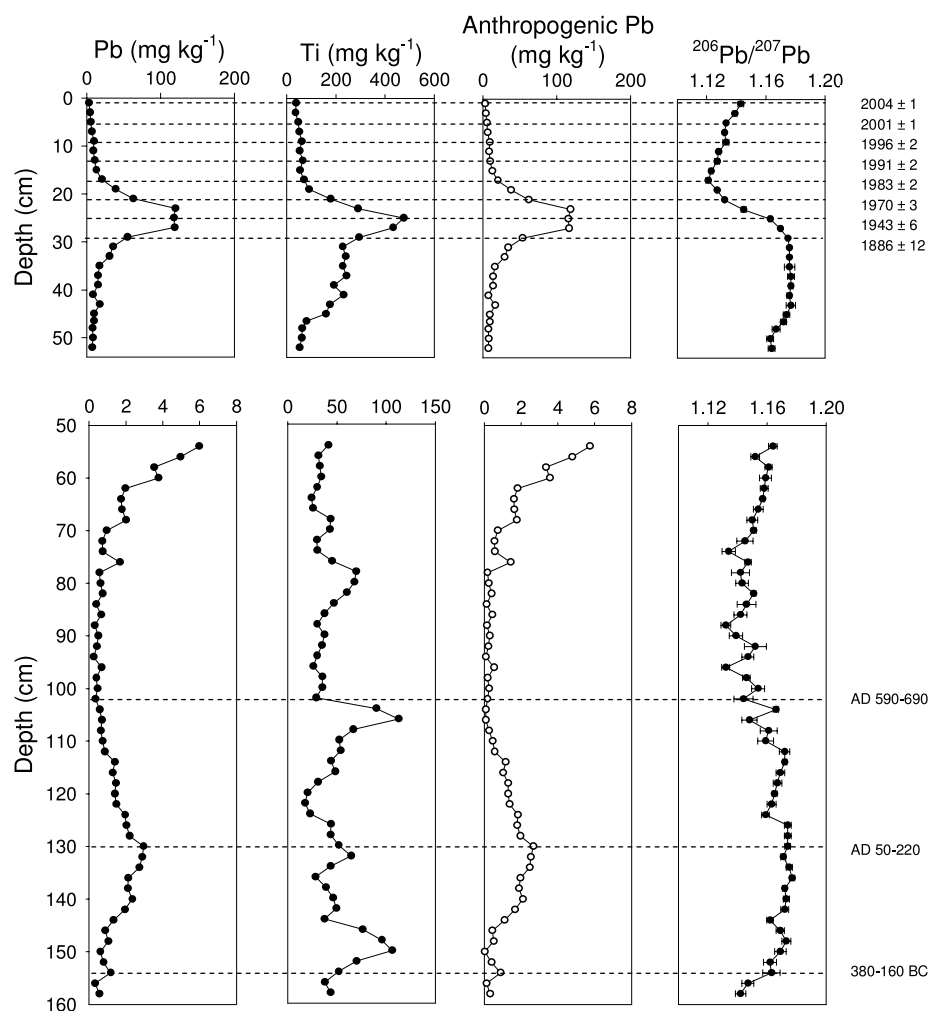


Figure 4. Profiles of Pb, Ti, and calculated anthropogenic Pb concentrations (calculated relative to Ti) (mg kg^{-1}) and measured $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in the combined ^{210}Pb - and ^{14}C -dated Turclossie Moss TM04CM-4 and TM04M-1 cores.

the long cores, FM01CM-1, RM03CM-2, TM04CM-4 and CM04CM-1 were $1.1 \pm 0.2 \text{ mg kg}^{-1}$ (71 to 53 cm), $0.55 \pm 0.18 \text{ mg kg}^{-1}$ (94 to 70 cm), $0.64 \pm 0.30 \text{ mg kg}^{-1}$ (113 to 69 cm) and $1.0 \pm 0.3 \text{ mg kg}^{-1}$ (106 to 80 cm), respectively (see Figures 2–5). These minimum concentrations generally occurred between the 4th and 10th centuries, after which concentrations increased again. Maximum total Pb concentrations and their corresponding depths and date ranges in cores from each of the sites are shown in Table 3. Total Pb concentrations in the 14–16, 16–18 and 18–20 cm CM04CM-1 sections were unusually high compared with those in CM04M (see Figure 5), suggesting that these sections may have been unduly or unrepresentatively contaminated, perhaps as a consequence of an isolated chance event, and they were excluded from interpretations of anthropogenic enrichments and historical trends.

3.2. Ti and Anthropogenic Pb Concentration Profiles

[12] Concentrations of Ti increased less markedly than those of Pb. The lowest measured mean Ti concentrations

(and their corresponding depths), in each of the long cores, FM01CM-1, RM03CM-2, TM04CM-4 and CM04CM-1, were $36 \pm 6 \text{ mg kg}^{-1}$ (59 to 52 cm), $20 \pm 2 \text{ mg kg}^{-1}$ (58 to 44 cm), $34 \pm 7 \text{ mg kg}^{-1}$ (77 to 53 cm) and $38 \pm 9 \text{ mg kg}^{-1}$ (68 to 52 cm), respectively (see Figures 2–5). These minimum concentrations occurred at various times between the 5th and 11th centuries. The highest measured Ti concentrations (up to 640 mg kg^{-1}) in cores from each of the bogs dated to the first half of the 20th century, with the exception of the maxima between the early 13th and mid-20th centuries and late 6th and early 10th centuries in the CM04CM-1 core (see Figures 2–5). These early Ti concentration maxima in CM04CM-1 are probably attributable to deposition of local soil dust arising from human activity, as supported by pollen analysis data for a separate core collected from CM by Dumayne-Peaty [1999]. There is very little difference between the measured total Pb concentrations and calculated anthropogenic Pb concentrations in the top part of the cores, i.e., the calculated lithogenic Pb

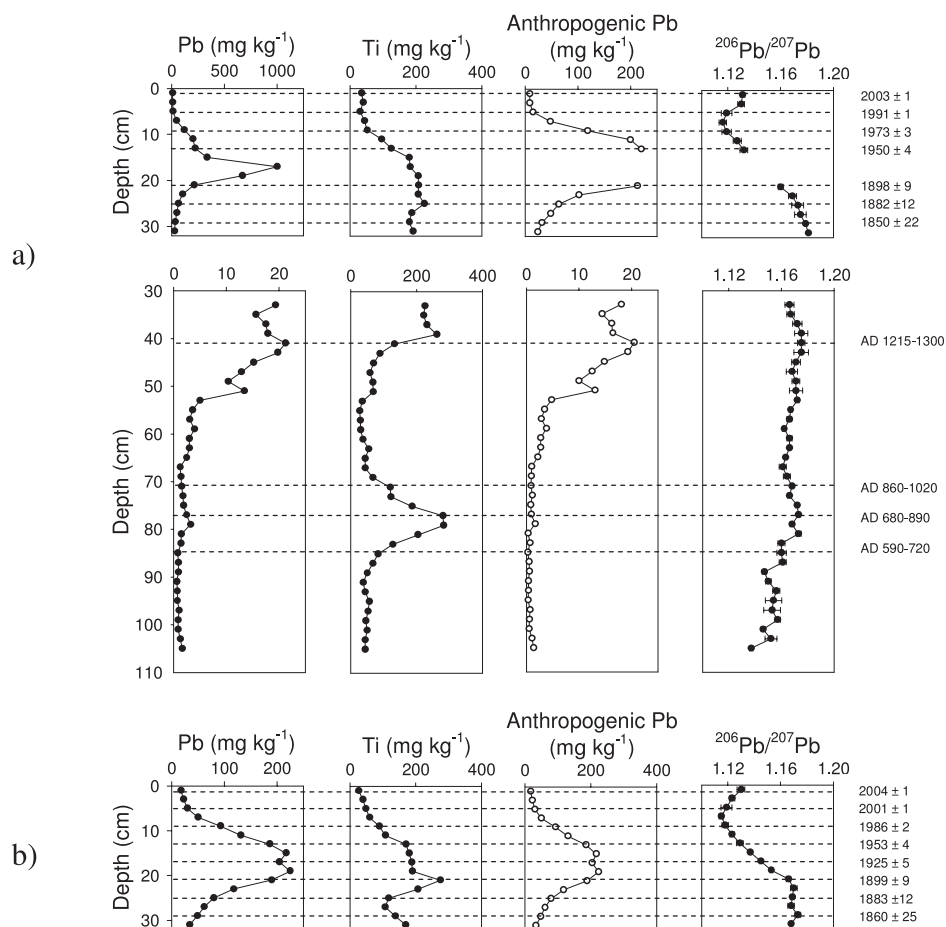


Figure 5. Profiles of Pb, Ti, and calculated anthropogenic Pb concentrations (calculated relative to Ti) (mg kg^{-1}) and measured $^{206}\text{Pb}/^{207}\text{Pb}$ ratio (a) in the ^{210}Pb - and ^{14}C -dated Carsegowan Moss CM04CM-1 core (omitting outlier values between 14 and 20 cm) and (b) in the ^{210}Pb -dated Carsegowan Moss CM04M core.

concentrations in the top part of the cores are very small in comparison (see Figures 2–5).

3.3. Profiles of $^{206}\text{Pb}/^{207}\text{Pb}$ Ratios

[13] The mean $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in the zones containing Pb concentration peaks at depth in the FM01CM-1 and TM04CM-4 cores were 1.176 ± 0.003 (102 to 71 cm) and

1.170 ± 0.005 (145 to 113 cm), respectively (see Figures 2a and 4). The mean $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in the zones of minimum Pb concentrations in each of the long cores, FM01CM-1, RM03CM-2, TM04CM-4 and CM04CM-1, were 1.164 ± 0.006 (71 to 53 cm), 1.156 ± 0.007 (94 to 70 cm), 1.148 ± 0.010 (113 to 69 cm) and 1.154 ± 0.009 (106 to 80 cm), respectively (see Figures 2–5). In the

Table 3. Maximum Total (and Anthropogenic) Pb Concentrations and Their Corresponding Depths, Date Ranges, and $^{206}\text{Pb}/^{207}\text{Pb}$ Ratios for Cores From Each of the Sites

Site	Core	Maximum Total (Anthropogenic) Pb Concentrations, mg kg^{-1}	Midpoint Depth or Depth Interval of Maximum Pb Concentrations, cm	Date Range of Maximum Pb Concentrations (A.D.)	Corresponding $^{206}\text{Pb}/^{207}\text{Pb}$ Ratios at Maximum Pb Concentrations
Flanders Moss (FM)	FM01CM-1	264 (262)	8.5	1948 ± 10	1.160 ± 0.002
	FM04-1-M	193 (191)	13.5	1955 ± 3	1.158 ± 0.000
The Red Moss of Balerno (RM)	RM03CM-1	255 (252)	12	1948 ± 12	1.164 ± 0.003
	RM03CM-2	369 (366)	9	1956 ± 8	1.159 ± 0.001
Turclossie Moss (TM)	TM04M-1	120 (119)	28 to 22	between ca. 1896 and 1967	decrease from 1.170 to 1.145
Carsegowan Moss (CM)	CM04CM-1	1000 (n/a)	17	n/a	n/a
	CM04M	range 205–225 (204–224)	20 to 14	between ca. 1903 and 1943	decrease from 1.153 to 1.137

uppermost sections of each of the cores, $^{206}\text{Pb}/^{207}\text{Pb}$ ratios remained fairly constant (~ 1.165 – 1.177) before decreasing to minimum values (~ 1.112 – 1.134). Subsequent increases in the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (to ~ 1.130 – 1.149) were then observed at the surface of each of the cores (except FM01CM-1). The $^{206}\text{Pb}/^{207}\text{Pb}$ ratio values during the Pb concentration maxima are shown in Table 3.

4. Discussion

4.1. Comparison of Historical Trends in Atmospheric Pb Deposition Profiles for the Scottish Sites

4.1.1. Pre-Roman and Roman Period

[14] Depths between 106 and 71 cm in FM01CM-1 (for which 94–96 cm and 91–93 cm were dated at ca. 210–40 B.C. and 85–86 cm was dated at ca. A.D. 20–220) and 159 and 113 cm in TM04CM-4 (for which 155–157 cm was dated at ca. 380–160 B.C.) corresponded to pre-Roman (pre-A.D. 43) and Roman (A.D. 43–410) periods (see Figures 2a and 4). Between 102 and 71 cm in FM01CM-1 and 145 and 113 cm in TM04CM-4, anthropogenic Pb concentration peaks during the pre-Roman/Roman period were found with maxima of 4.4 mg kg^{-1} at 90–91 cm (ca. 210–40 B.C.) and 2.7 mg kg^{-1} at 129–131 cm (ca. A.D. 50–220) in FM01CM-1 and TM04CM-4, respectively.

[15] For the peat sections encompassing the anthropogenic Pb concentration peaks in FM01CM-1 (102 to 71 cm) and TM04CM-4 (145–113 cm) (see Figures 2a and 4), the “weighted” average $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$, and $^{208}\text{Pb}/^{207}\text{Pb}$ ratio values, which take differing total Pb concentrations and sectional dry weights into account, were 1.176, 2.088, and 2.453, and 1.171, 2.100, and 2.458, respectively. At a bog in Loch Laxford (northwest Scotland) (see Figure 1), undated samples between ~ 62 and 76 cm depth, with Pb concentrations $\sim 1 \text{ mg kg}^{-1}$, had an average $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.166 ± 0.003 [Weiss *et al.*, 2002], comparable to those found between 125 and 113 cm (pre-Roman/Roman period samples) in the TM04CM-4 core.

4.1.2. Post-Roman and Medieval Period

[16] Depths between 71 and 33 cm in FM01CM-1, 96 and 40 cm in RM03CM-2, 113 and 53 cm in TM04CM-4 and 106 and 32 cm in CM04CM-1 corresponded to post-Roman and medieval periods. During the post-Roman/early medieval period (between ca. 5th and 10th centuries), anthropogenic Pb concentrations were at their lowest (0.53 – 1.23 mg kg^{-1}) (see Figures 2–5), reflecting the decline in metallurgical activities after the fall of the Roman Empire (ca. A.D. 410). The corresponding measured $^{206}\text{Pb}/^{207}\text{Pb}$ ratios during these periods, with values ranging from 1.155 to 1.175 in FM01CM-1, 1.147 to 1.172 in RM03CM-2, 1.132 to 1.172 in TM04CM-4 and 1.137 to 1.173 in CM04CM-1, were significantly less radiogenic than those found during the pre-Roman/Roman periods in the FM and TM cores. These less radiogenic values could reflect contributions, albeit relatively minor, from long-range atmospheric deposition of Pb from metallurgical processing of the Rio Tinto (southwest Spain) Pb ores ($^{206}\text{Pb}/^{207}\text{Pb}$ ratios ~ 1.16) [Stos-Gale *et al.*, 1995] by the Visigods, who founded an economically prosperous kingdom at the end of the

Roman Empire that lasted until the end of the 6th century [Martinez-Cortizas *et al.*, 1997] (see section 4.2.1).

[17] Increases in anthropogenic Pb concentration at each of the four sites during the late medieval period (generally between ca. 9th and 15th centuries) (see Figures 2–5), reflect the growth in Pb mining and smelting activities, especially in continental Europe (see section 4.2.2). The magnitude of these medieval Pb concentration increases varied in the order $\text{CM} > \text{FM}$, $\text{RM} > \text{TM}$, perhaps reflecting the closer proximity of the most southerly site, CM, to English medieval Pb mining and smelting sources. The corresponding $^{206}\text{Pb}/^{207}\text{Pb}$ ratios, ranging from 1.165 to 1.171 in FM01CM-1, 1.150 to 1.176 in RM03CM-2, 1.134 to 1.164 in TM04CM-4 and 1.162 to 1.175 in CM04CM-1 (see Figures 2–5), were generally higher than those in the sections corresponding to the anthropogenic Pb concentration minima.

4.1.3. Industrial and Postindustrial Period

[18] Depths between 33 and 0 cm in FM01CM-1 and FM04-1-M, 40 and 0 cm in RM03CM-2, 31 and 0 cm in RM03CM-1, 53 and 47 cm in TM04CM-4, 47 and 0 cm in TM04M, and 32 and 0 cm in CM04CM-1 and CM04M corresponded to the industrial (ca. A.D. 1650–1970) and postindustrial (ca. A.D. 1970 to present) periods (see Figures 2–5). Marked increases in anthropogenic Pb concentrations were found in cores from each of the sites during the industrial period. Between the mid-17th and early 20th centuries, initial concentration increases and fairly constant $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (mean values ranging from ~ 1.165 – 1.176) in the FM, RM and TM cores (see Figures 2–4) are largely attributable to emissions from the mining and smelting of Pb ores from Wanlockhead and Leadhills in southwest Scotland ($^{206}\text{Pb}/^{207}\text{Pb}$ ratio $\sim 1.170 \pm 0.003$) [Sugden *et al.*, 1993; Rohl, 1996; Cloy *et al.*, 2005]. The slightly higher $^{206}\text{Pb}/^{207}\text{Pb}$ ratio values (mean 1.176 ± 0.002) between ca. A.D. 1650 and 1896 in the TM04M-1 core, consistent with those in sister core TM04CM-2, suggest small contributions from other sources of Pb, such as coal combustion ($^{206}\text{Pb}/^{207}\text{Pb} \sim 1.181$) [Farmer *et al.*, 1999]. Interestingly, for the most southerly site, CM, the fall in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios to values of 1.160 and 1.166 at ca. A.D. 1900 in CM04CM-1 and CM04M, respectively (see Figure 5), well before the introduction of leaded petrol, may well indicate the early influence of the use of imported Pb ores (e.g., Australian, $^{206}\text{Pb}/^{207}\text{Pb} \sim 1.04$) in more southern parts of Britain [Day and Tylecote, 1991]. Similar trends were recorded in archival herbage [Bacon *et al.*, 1996] from England, thus providing further evidence that the earlier onset of the decrease in $^{206}\text{Pb}/^{207}\text{Pb}$ at CM, compared with the other sites, may be related to the influence from the south.

[19] In cores from each of the sites, anthropogenic Pb concentrations increased to maximum values (up to 370 mg kg^{-1}), while the corresponding $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratios decreased (to 1.137) (see Table 3 and Figures 2–5), reflecting the decline in Scottish Pb mining after the 19th century and the increasing influence of the use of imported Australian Pb ore, predominantly via car exhaust emissions from the 1930s. Intermediate $^{206}\text{Pb}/^{207}\text{Pb}$ ratio values (see Figures 2–5 and Table 3) also suggest significant contribu-

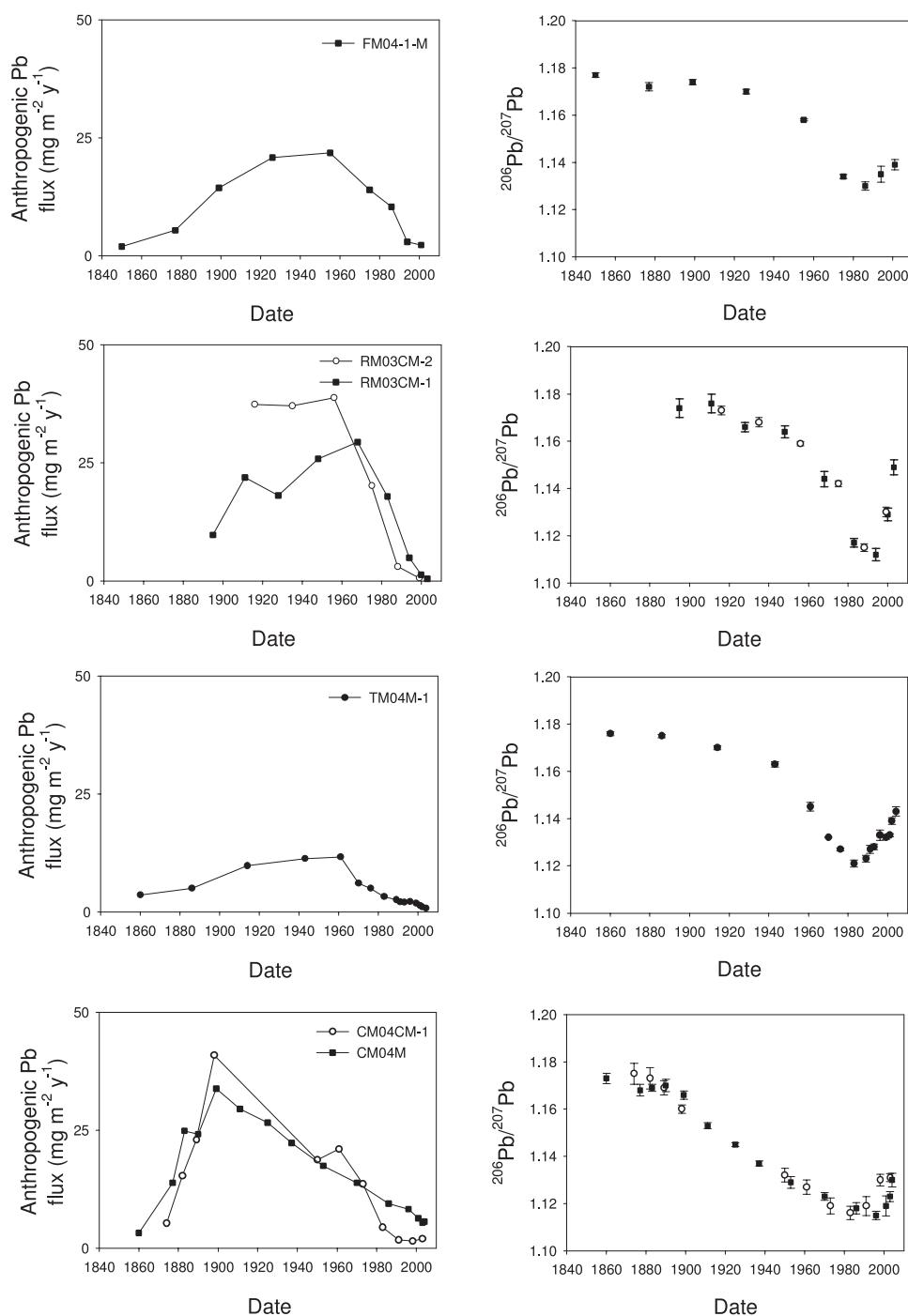


Figure 6. Calculated atmospheric depositional fluxes of anthropogenic Pb and measured $^{206}\text{Pb}/^{207}\text{Pb}$ ratios for cores from each peat bog site versus ^{210}Pb -derived dates since A.D. 1840.

tions from other sources of Pb, such as coal combustion. After the late 1960s, anthropogenic Pb concentrations declined, with further decreases in the corresponding $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (to 1.112, between the early 1980s and mid-1990s) (see Figures 2–5), reflecting the decreasing influence of coal combustion and increasing influence of vehicle exhaust emissions of Pb during the postindustrial period (after ca. A.D. 1970). In recent years, anthropogenic

Pb concentrations continued to fall while the corresponding $^{206}\text{Pb}/^{207}\text{Pb}$ ratios increased (to ~ 1.13 – 1.15) (see Figures 2–5), reflecting the steep fall in Pb emissions from car exhausts as the use of unleaded petrol became increasingly predominant after the mid-1990s, followed by the ban on leaded petrol in the UK from A.D. 2000. The increase in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios to the present also reflects the importance of other sources of Pb (e.g., waste incineration) relative to

petrol at this time. Similar trends were found at Loch Laxford (northwest Scotland) (see Figure 1), i.e., maximum Pb enrichment at ca. A.D. 1960 and decreases in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios after ca. A.D. 1930, reaching a minimum (~ 1.115) at ca. A.D. 1988 [Weiss *et al.*, 2002].

[20] Calculated ‘accumulation rates’ of anthropogenic Pb in the peat were assumed to be the same as atmospheric depositional fluxes of anthropogenic Pb. The timings of the maximum anthropogenic Pb fluxes at each of the sites (Figure 6), with the exception of the significantly earlier increases at CM, were in close agreement, fluxes decreasing in the order $\text{CM} > \text{RM} > \text{FM} > \text{TM}$ (as did post-1800 inventories of 2.7–5.0, 2.5–4.3, 2.1–3.6, and 1.2 g m^{-2} , respectively), perhaps reflecting the closer proximity of CM to major Pb pollution sources in England and the closer proximity of the RM and FM sites to industrial/transportation sources of Pb contamination in the heavily populated central belt of Scotland. A depositional Pb flux peak of $\sim 50 \text{ mg m}^{-2} \text{ a}^{-1}$ at ca. A.D. 1940 in a peat core from South Drumbo Hill (see Figure 1) [MacKenzie *et al.*, 1998], also situated in the central belt of Scotland, was in agreement with those at FM and RM (see Figure 6). MacKenzie *et al.* [1997] also found a higher maximum Pb flux ($\sim 37 \text{ mg m}^{-2} \text{ a}^{-1}$) at FM relative to that ($\sim 5.0 \text{ mg m}^{-2} \text{ a}^{-1}$) in a core from a remote site at North Uist (northwest Scotland) (see Figure 1), again consistent with trends in the Scottish peat bogs investigated here. As a consequence of topographical and plant compositional features that affect the efficiency of particle trapping and retention [Bindler *et al.*, 2004], there may be significant variations in apparent fluxes across the same bog, as suggested by significant variations at RM (see Figure 6). Also, maximum Pb fluxes ranging from 20–60 $\text{mg m}^{-2} \text{ a}^{-1}$ have previously been reported for FM [Farmer *et al.*, 1997, 2006; MacKenzie *et al.*, 1997]. The similar key features in the temporal trends in the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios at each of the sites (see Figure 6), however, indicate that the sites were influenced by similar sources of Pb contamination during the industrial and postindustrial periods (see section 4.2.3), supported by additional evidence from Scottish lake sediment cores and archival herbarium moss [Farmer *et al.*, 1996, 1997, 2002, 2006; Eades *et al.*, 2002].

4.2. Isotopic Comparison of Historical Trends in Sources of Atmospheric Pb Deposition in Scotland With Those in Other Western European Countries and Greenland

[21] In general, the main features of the trends in Pb concentration and, to some extent, $^{206}\text{Pb}/^{207}\text{Pb}$ ratio recorded from ca. 500 B.C. to A.D. 2004 at the four Scottish peat bog sites were in broad agreement with those found in other environmental archive records from other western European countries and Greenland, as summarized by Renberg *et al.* [2001] and Bindler [2006] for the period from 2000 B.C. to A.D. 2000 for Swedish, Swiss and Spanish peat bogs, Swedish lake sediments and Greenland ice. The following three sections consider in more detail the sources of anthropogenic Pb deposited in Scotland, western Europe and Greenland during each of three different time periods: pre-Roman/Roman, post-Roman/medieval and industrial/postindustrial.

4.2.1. Pre-Roman and Roman Period

[22] The individual $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios of the Scottish pre-Roman/Roman FM01CM-1 and TM04CM-4 peat samples are plotted along with those of various European Pb ores and pre-Roman/Roman samples (range ca. 570 B.C.–A.D. 510) of Greenland ice, Irish lake sediment, and Faroese, English, Belgian, Swiss, French and Spanish peat as shown and described in Figures 7a–7c.

[23] The FM01CM-1 samples are in better agreement with ores of British origin than those from the major Spanish mines (see Figures 7a and 7b), supporting the findings at Lindow Bog in the northwest of England (see Figures 1 and 7c) [Le Roux *et al.*, 2004], a country where the influence of local Pb production has been recognized (see Figure 1) [Lee and Tallis, 1973; West *et al.*, 1997]. While atmospheric transport of Pb from mining and smelting of minor Belgian ores (see Figures 7a and 7b) is unlikely to have been significant for FM01CM-1, the TM04CM-4 samples appear to have been influenced by both British and Spanish ores (see Figures 7a and 7b), suggesting deposition at TM from long-range atmospheric transport of Pb associated with Pb production in the Rio Tinto mining district of southwest Spain. There may have been masking of long-range atmospheric transport at the more southerly FM and English locations by dominating, often local, British sources. In western Irish lake sediments (see Figure 1), possible contributions from Spanish, as well as British, Pb ore sources (see Figure 7c) were attributed to occasional meteorological conditions of southerly, rain-accompanied winds and efficient wet deposition of Pb [Schettler and Romer, 2006].

[24] The deposition of atmospheric Pb originating mainly from southwestern (e.g., Rio Tinto) and southeastern Spain was considered significant for anthropogenic Pb in Greenland ice [Rosman *et al.*, 1997] and in Swiss peat at Etang de la Gruère [Shotyik *et al.*, 1998], although Figures 1 and 7c show that other sources may also have contributed. In contrast, Monna *et al.* [2004a, 2004b] showed that the Pb isotopic signatures ($^{206}\text{Pb}/^{207}\text{Pb}$ ratios ~ 1.18 – 1.19) in peat from the Port-des-Lambert bog in central France (see Figure 1) and at the Quinto Real peat bog in southwest France (see Figures 1 and 7c) were incompatible with those of the Rio Tinto district ($^{206}\text{Pb}/^{207}\text{Pb}$ ratios ~ 1.16) [Stos-Gale *et al.*, 1995], attributing the difference to masking by deposition arising from the use of local French Pb ores (see Figures 7a and 7c). At Misten bog in southeast Belgium (see Figure 1), however, where Pb contamination ($^{206}\text{Pb}/^{207}\text{Pb}$ ratios ~ 1.176) during the early Roman Empire was attributed to local Pb–Zn ore ($^{206}\text{Pb}/^{207}\text{Pb}$ ratio range 1.16–1.18) mining activities [De Vleeschouwer *et al.*, 2007], the Pb isotopic composition of the later peat samples (Figure 7c) suggests significant contributions from long-range transport and deposition of Spanish Pb (see Figure 7c). In Spain itself, while enrichments of Pb during the Roman period in a peat core from Penido Vello bog in northwest Spain (see Figures 1 and 7c) have been attributed to major Spanish Pb mining and smelting activities, the Pb isotopic composition of the peat (see Figure 7c) may also have been influenced by natural radiogenic sources such as local soil dust of markedly different isotopic composition (e.g., Spanish pre-

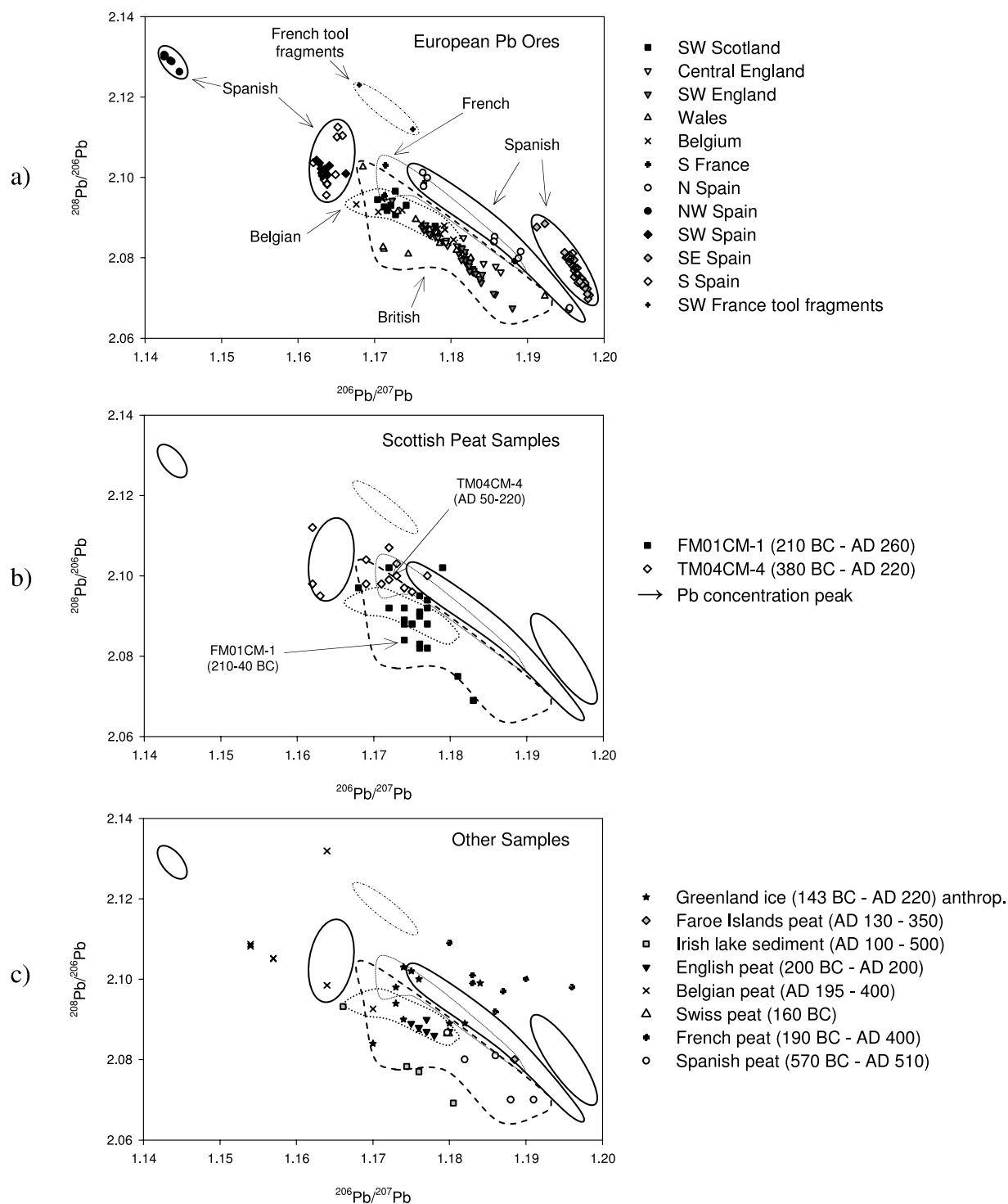


Figure 7. Plot of $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{206}\text{Pb}/^{207}\text{Pb}$ ratios for (a) European Pb ores [Stos-Gale et al., 1995; Rohl, 1996; Monna et al., 2004b; Kylander et al., 2005; De Vleeschouwer et al., 2007], (b) pre-Roman/Roman FM01CM-1 and TM04CM-4 peat samples, and (c) pre-Roman/Roman samples from Greenland ice (calculated anthropogenic) [Rosman et al., 1997], Irish lake sediment [Schettler and Romer, 2006], and Faroe Islands [Shotyk et al., 2005], English [Le Roux et al., 2004], Belgian [De Vleeschouwer et al., 2007], Swiss [Shotyk et al., 1996], French [Monna et al., 2004b], and Spanish [Kylander et al., 2005] peat.

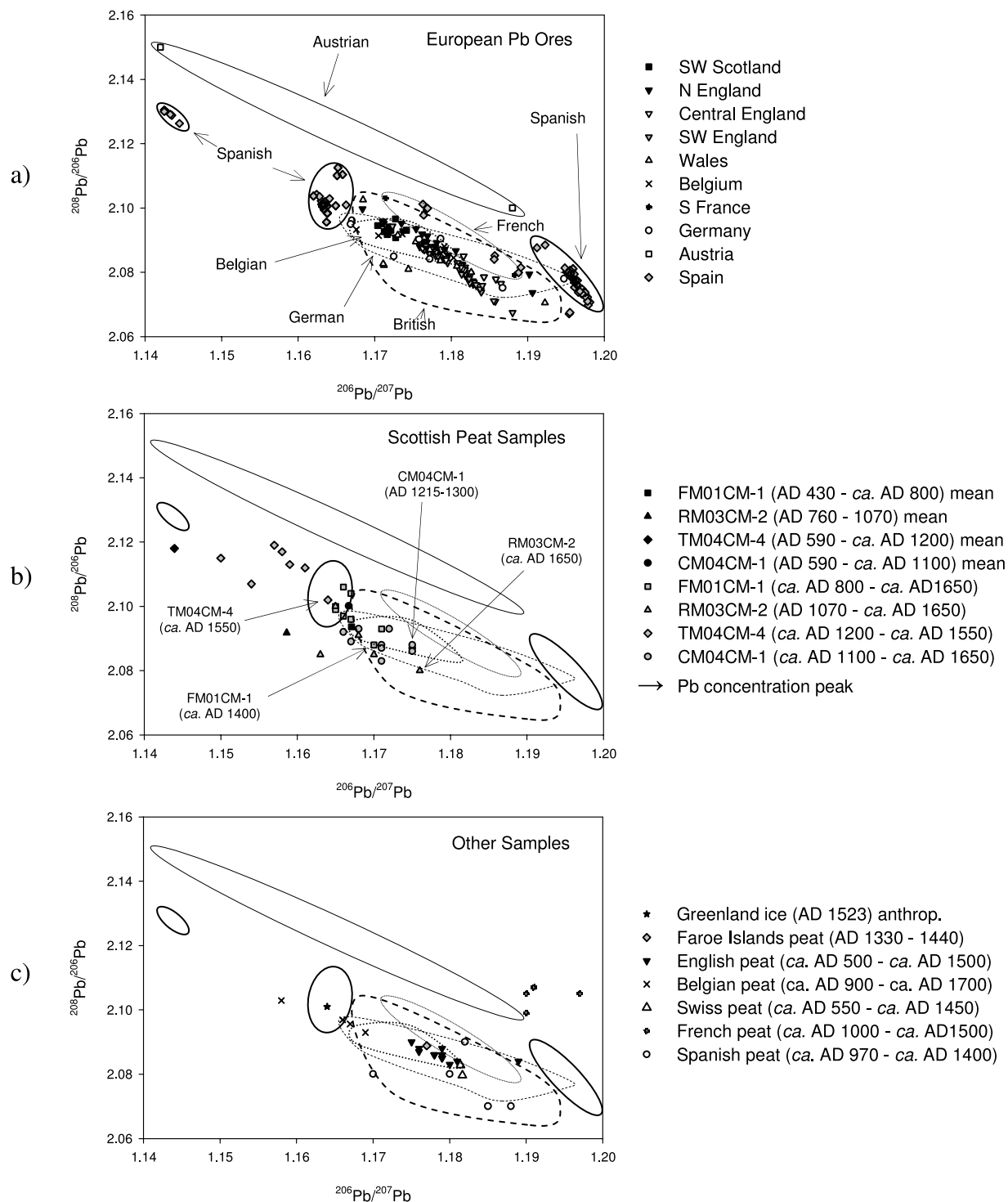


Figure 8. Plot of $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{206}\text{Pb}/^{207}\text{Pb}$ ratios for (a) European Pb ores [Stos-Gale *et al.*, 1995; Rohl, 1996; Monna *et al.*, 2000; Kylander *et al.*, 2005; De Vleeschouwer *et al.*, 2007], (b) post-Roman/early medieval and late medieval/early modern FM01CM-1, RM03CM-2, TM04CM-4 and CM04CM-1 peat samples, and (c) post-Roman, medieval and early modern samples from Greenland ice (calculated anthropogenic) [Rosman *et al.*, 1997], and Faroe Islands [Shotyk *et al.*, 2005], English [Le Roux *et al.*, 2004], Belgian [De Vleeschouwer *et al.*, 2007], Swiss [Shotyk *et al.*, 1996, 2002b], French [Monna *et al.*, 2004b], and Spanish [Kylander *et al.*, 2005] peat.

Pb-pollution aerosol $^{206}\text{Pb}/^{207}\text{Pb}$ 1.255 ± 0.026 [Kylander et al., 2005]. In southern Sweden, in three peat bogs (Store Mosse, Trolls Mosse and Öneby Mosse) (see Figure 1) for which full isotopic composition data are not available, Brännvall et al. [1997] suggested that the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of ~ 1.175 associated with a Roman Pb concentration peak (dated at ca. A.D. 0) could result from the long-range transport of both soil dust and metallurgically derived atmospheric pollution from continental Europe.

4.2.2. Post-Roman and Medieval Period

[25] The $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios of the Scottish post-Roman/early medieval and later medieval/early modern FM01CM-1, RM03CM-2, TM04CM-4 and CM04CM-1 peat samples are plotted along with those of various European Pb ores and post-Roman, medieval and early modern (range ca. A.D. 450–1700) samples of Greenland ice and Faroese, English, Belgian, Swiss, French and Spanish peat as shown and described in Figures 8a–8c.

[26] The isotopic composition of the Scottish post-Roman/early medieval samples is generally in agreement with Spanish and British Pb ores (see Figures 8a and 8b), the less radiogenic values compared with the Roman period possibly reflecting deposition from long-range atmospheric transport of Pb from metallurgical processing of Spanish (e.g., Rio Tinto) Pb ores by the Visigods (see section 4.1), also noted in peat from northwest Spain [Martinez-Cortizas et al., 1997] and southeast Belgium [De Vleeschouwer et al., 2007] as well as Irish lake sediments [Schettler and Romer, 2006]. In these times of lower Pb concentrations, however, contributions from soil dust are likely to have been more important but the limited data (none for Britain) that exist on its natural Pb isotopic composition show large heterogeneity, e.g., pre-Pb-pollution aerosol $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of 1.255 ± 0.026 [Kylander et al., 2005], 1.199 ± 0.000 [Shotyk et al., 2001], $1.198\text{--}1.212$ [Klaminder et al., 2003] and 1.201 ± 0.030 [Rosman et al., 1997] for Spain, Switzerland, Sweden and Greenland, respectively.

[27] The more radiogenic isotopic composition of the Scottish late medieval/early modern samples is in apparent agreement with British, Belgian, German, Austrian and Spanish Pb ores (see Figures 8a and 8b) and also with peat $^{206}\text{Pb}/^{207}\text{Pb}$ ratio values of $\sim 1.155\text{--}1.170$ at ca. A.D. 1500 from Dumme Mosse and Traneröd Mosse [Klaminder et al., 2003] (see Figure 1) and, from ca. A.D. 1000, of $\sim 1.155\text{--}1.175$ in Store Mosse, Trolls Mosse and Öneby Mosse [Brännvall et al., 1997] in southern Sweden (see Figure 1). In contrast, English Pb ores appear to have been the predominant source of Pb at Lindow bog (northwest England) (see Figures 1 and 8c) [Le Roux et al., 2004].

[28] The isotopic composition of anthropogenic Pb in Greenland ice at A.D. 1523 (see Figures 1 and 8c) reflects long-range transport of European (predominantly southwest

Spanish) aerosols [Rosman et al., 1997]. Emissions from the production of Pb in Germany ($^{206}\text{Pb}/^{207}\text{Pb}$ ratio range $1.168\text{--}1.195$) [Monna et al., 2000] for silver production are thought to have influenced the isotopic composition of Pb at Etang de la Gruère bog in west Switzerland (see Figures 1 and 8c) [Shotyk et al., 1998] and, more locally in the Harz area, the enrichment of Pb at Sonnenberger bog (see Figure 1) in central Germany in the 12th and 13th centuries A.D. [Kempter and Frenzel, 2000]. Local mining and smelting influences appear to have been dominant for Pb at Misten bog in southeast Belgium [De Vleeschouwer et al., 2007] and at Quinto Real peat bog in southwest France [Monna et al., 2004b] but perhaps less so at Penido Vello bog in northwest Spain [Kylander et al., 2005] (see Figures 1 and 8c). Overall, the wide range of Pb isotopic composition data in different records for the preindustrial medieval period from western Europe and Greenland reflects the variety of ores being mined across Europe [Settle and Patterson, 1980; Hong et al., 1994; Bindler, 2006].

4.2.3. Industrial and Postindustrial Period

[29] The individual $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios of the Scottish industrial and postindustrial FM01CM-1, FM04-1-M, RM03CM-1, RM03CM-2, TM04M-1, CM04CM-1, and CM04M peat samples are plotted along with those of various European Pb ores and industrial/postindustrial (range primarily ca. A.D. 1800–2004) samples of Faroese, Belgian, Swiss, French and Spanish peat as shown and described in Figures 9a–9c.

[30] The most striking feature of the three-isotope plots for both Scottish (Figure 9b) and other European (Figure 9c) peat samples is, of course, the influence of imported Australian Pb (Figure 9a) in the 20th century, primarily through the use of leaded petrol (Figure 9a), as reflected in the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio minima (to as low as 1.11) recorded typically in the 1980s prior to the introduction of unleaded petrol. In peat cores from southern Greenland and Denmark (see Figure 1), however, minimum $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratios occurred at ca. 1960 A.D. and the late 1970s, respectively [Shotyk et al., 2003], although Bindler [2006] has suggested that slight differences in chronologies could arise as a result of different methods (^{210}Pb and “bomb” ^{14}C dating) used to date recent peat deposits. The other Pb source end-members, of higher $^{206}\text{Pb}/^{207}\text{Pb}$ ratio, include incinerator fly ash, coal combustion, and indigenous European Pb ores (Figure 9a).

[31] Renberg et al. [2001] have noted that records of Pb contamination during the industrial and postindustrial periods can vary within Europe depending upon factors such as the relative extent of mining/smelting and coal combustion, as well as the dates of introduction/reduction/withdrawal of leaded petrol and the implementation of stricter emission regulations. The Scottish peat records of Pb concentration

Figure 9. Plot of $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{206}\text{Pb}/^{207}\text{Pb}$ ratios for (a) European [Stos-Gale et al., 1995; Rohl, 1996; Monna et al., 2000; Kylander et al., 2005; De Vleeschouwer et al., 2007] and Australian [Sugden et al., 1993] Pb ores, British coals [Farmer et al., 1999], leaded petrol [Farmer et al., 2000], and incinerator fly ash [Monna et al., 1997], (b) industrial/postindustrial FM01CM-1, FM04-1-M, RM03CM-1, RM03CM-2, TM04M-1, CM04CM-1 and CM04M peat samples, and (c) industrial/postindustrial samples from Faroe Islands [Shotyk et al., 2005], Belgian [De Vleeschouwer et al., 2007], Swiss [Shotyk et al., 1996, 2002b], French [Monna et al., 2004b] and Spanish [Kylander et al., 2005] peat.

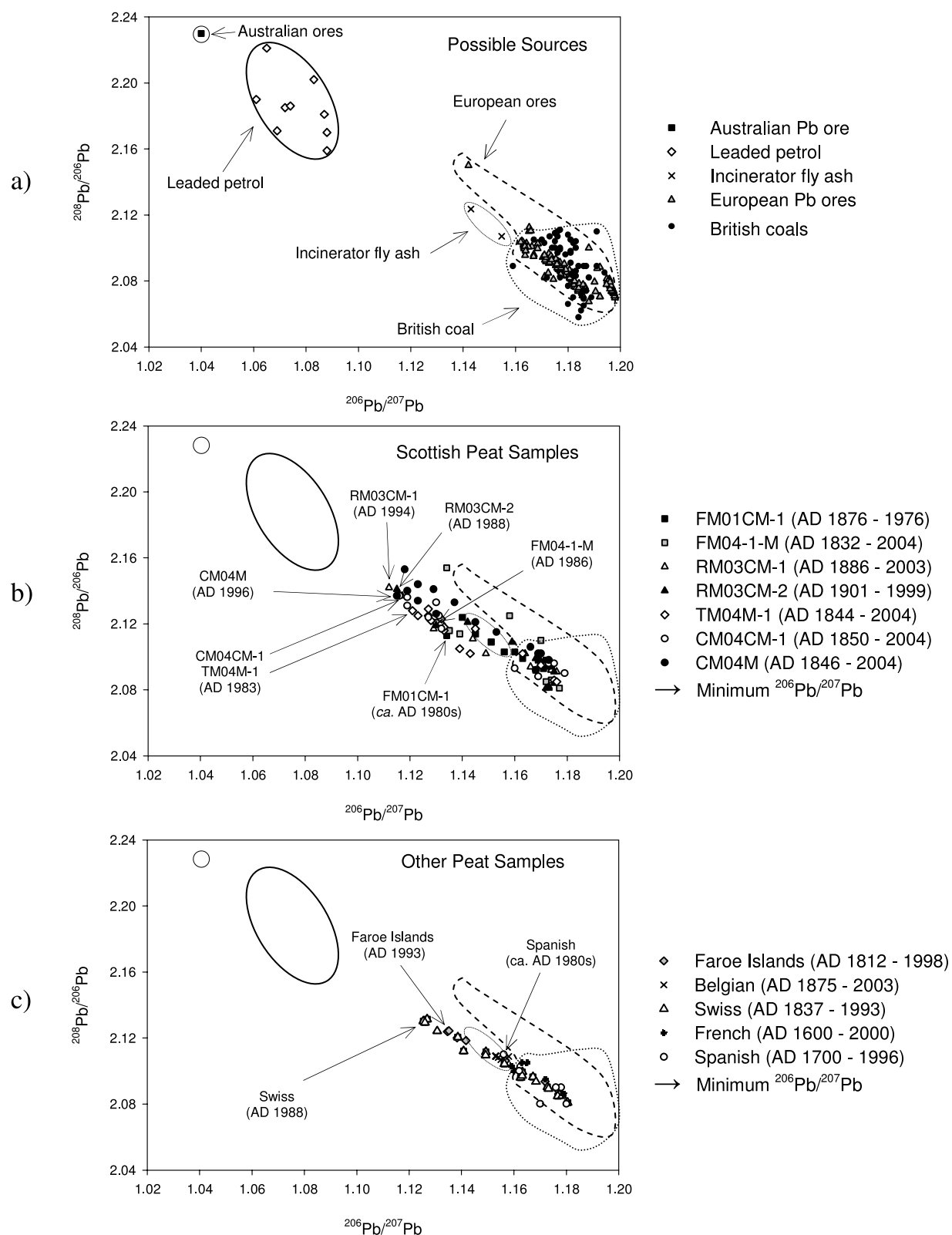


Figure 9

and isotopic composition (Figures 2–5 and Table 3) show that the maximum extent of Pb contamination predated the maximum impact of Pb emissions from the use of leaded petrol, suggesting that other sources such as coal combustion emissions were significant, further supported by findings at Glensnaugh, an upland catchment in rural northeast Scotland [Farmer *et al.*, 2005]. Peat records from Etang de la Gruère (Switzerland), Storelung Mose (Denmark), Shetland, and Myrarnar (Faroe Islands) [Shotyk *et al.*, 2002b, 2003, 2004, 2005] (see Figure 1) also indicated that coal combustion emissions were significant in the industrial past. Post-1800 anthropogenic Pb inventories (range 1.2–5.0 g m⁻²) in Scottish peat cores generally exceeded those of Swedish (post-1890, 0.75–1.4 g m⁻², Store Mosse and Dumme Mosse) [Bindler *et al.*, 2004] and Swiss (post-1850, ~1.3 g m⁻², Etang de la Gruère) [Shotyk *et al.*, 2000; Le Roux *et al.*, 2005] peat cores.

5. Conclusions

[32] The general agreement in the major trends in atmospheric Pb deposition recorded in four Scottish peat bogs (FM, RM, TM and CM) during the last 2500 years suggests that the sites were influenced by similar sources of Pb contamination. During the pre-Roman and Roman periods, FM and TM were both influenced by the mining and smelting of local British Pb ores, although the relative influence of long-range atmospheric deposition from metallurgical activities in Spain may have been stronger at the more northerly TM. At all four sites, medieval increases in Pb contamination arising from European metallurgical activities were found. During the industrial and postindustrial periods, there were major increases in Pb contamination arising from the mining and smelting of British and imported Pb ores, coal burning and Australian-Pb-influenced car exhaust emissions at each of the sites, although earlier influence from the use of imported Pb ores was evident at CM. Levels of Pb contamination for each of the historical time periods were highest in the south (FM, CM) and lowest in the north (TM) of Scotland. Although there was general agreement with other environmental Pb archive records for Scotland and other countries in western Europe and Greenland, subtle variations in the timings and magnitude of anthropogenic Pb contamination and isotopic composition reflected influences of local and regional sources.

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